

Magnetism from lodestone to plastics

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Abstract : Magnetism abounds in dichotomies. Humans have wondered about and used magnetism since the discovery of lodestone more than four thousand years ago. This invited talk aims to review the developments of the magnetic phenomena. Special importance is attached to recent advances in magnetic materials such as magnetic multilayers, half metallic magnets, coexistence of ferromagnetism and superconductivity, spintronics and, last but not the least, photo induced magnetism in plastic materials.

Keywords : History of magnetism, magnetic multilayers, half metallic magnets, spintronics and photo induced magnetism.

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1. Brief history

Magnetism and magnetic phenomena have a long history [1] but still continue to be intriguing and exciting. They fascinate a school child and yet the understanding of the phenomena is closely associated with quantum theory. Although magnetic phenomena have paved way for huge industries, its understanding even in iron is not complete. The first application of the magnetic phenomena is the compass. This seemingly simple device is behind great geographical discoveries. Compass is believed to be known to Europeans by about 12th century, although there is some belief that it was known to the Chinese much earlier. The classical age in magnetism is dominated by C A Coulomb (1736-1806), S D Poisson (1781-1840), H C Oersted (1777-1851), A M Ampere (1775-1836) and Sir Humphrey Davy (1778-1829). In the 19th century, Michael Faraday (1791-1867) had contributed significantly to the magnetic phenomena. The laws of electromagnetic induction and Faraday effect (motion of the plane polarized light passing through a medium in a direction parallel to magnetization) are among his contributions. He studied magnetic phenomena in different substances and proclaimed that all substances would show some or other kind of magnetic phenomena. However, this 19th century genius did not have a formal training in science and it was believed that

his knowledge of mathematics was quite inadequate. It was another stalwart of the same century, J C Maxwell (1831-1879) who summarised Faraday's experiments. Maxwell's equations represent a beautiful summary of electromagnetic phenomena. They also represent the first unification of two fundamental fields, namely, the electric field and the magnetic field. P Curie studied the thermal properties of magnetic substances and showed that the magnetic susceptibility of paramagnetic substances is inversely proportional to the temperature. About ten years later, P. Langevin proceeded little further and expressed magnetization as a function of the magnetic field and temperature, which in the weak field limit, reduced to Curie's formula. The discovery of electron by J J Thomson ushered a new era in Physics.

The beginning of the modern era of magnetism coincided with the beginning of the quantum theory. Earlier, P Weiss developed the molecular field theory and tried to explain the magnetic hysteresis (a non-equilibrium property, based on the concepts ferromagnetic domains). Van Leeuwen proposed the vanishing diamagnetism of a classical ideal gas. The real breakthrough of the modern era began with the determination of the magnetic moment of an atom by Stern and Gerlach. In 1921, A H Compton proposed that electron possesses an intrinsic spin and a

resulting magnetic moment, in addition to the orbital angular momentum. Goudsmit and Uhlenbeck assigned the electron spin as $\hbar/2$. The spin matrices were introduced by Pauli, which bear his name. Other milestones in the development of magnetism are Heisenberg's exchange interaction, Ising model, Pauli paramagnetic susceptibility and Landau diamagnetic susceptibility of a free electron gas. By about 1930's, it became more or less certain that all kinds of materials show some or other kind of magnetism, predicted much earlier by Faraday. The magnetic phenomena described above were summarised in two classic books by Van Vleck [2] and Stoner [3] respectively. With the discovery of antiferromagnetism by Neel [4], the subject became more exciting. In 1936, Slater laid the foundation of itinerant electron magnetism [5–7], which explained the observed values of the atomic magnetic moment in transition metals, such as Fe, Co and Ni.

2. Indian contribution to magnetism

The early period of modern magnetism contained some significant contributions from D M Bose, C V Raman and K S Krishnan. D M Bose measured the magnetic susceptibility of a number of iron-group compounds and also studied the systematics in Pd, Pt and U during the early part of the second quarter of the twentieth century [2,8]. Around the same time, C V Raman also published a number of papers on diamagnetism and magnetic birefringence [9]. During 1929–33, Prof. Krishnan was in Dacca. Here he turned his attention to the subject of magnetic properties of crystals in relation to their structure and developed elegant and precise experimental techniques to measure the magnetic anisotropy of dia- and para-magnetic crystals. He published several papers and notes in the subject in collaboration with B C Guha, S Banerjee and N C Chakravorty [10]. In 1933, he returned back to Calcutta (as Mahendralal Sircar Professor of Physics at the Indian Association for the Cultivation of Science) where he studied quite vigorously magnetic properties of the salts of rare earth and iron groups. His work on the diamagnetism of graphite showed large anisotropy, maximum contribution being along the C-axis.

3. Magnetism of Bloch electrons

The problem of the magnetic susceptibility of Bloch electrons occupied several theorists, more seriously since early sixties (see refs. 11 and 12 for detailed reviews). The problem was studied by Blount, Roth, Yafet, Kjeldass and Kohn, Luttinger and Kohn, Misra and Roth, Misra and Kleinman, Misra *et al* and Tripathi. The orbital susceptibility derived by Misra and Roth was applied to calculate the

quantity in some simple metals. Misra and Kleinman [11] considered both the spin and orbital natures of electrons and have also taken into account the effects of spin-orbit interactions on the susceptibility (χ_{MK}). Their formula for the susceptibility is written as

$$\chi_{MK} = \chi_s + \chi_0 + \chi_{so}, \quad (1)$$

where χ_s is the effective Pauli spin susceptibility which includes the effect of the spin-orbit interaction through the square of the effective g -factor. χ_0 is the orbital susceptibility. χ_{so} is a distinct contribution which arises from the effect of the spin orbit interaction on the orbital motion of Bloch electrons. Many body effects on these contributions were considered by Misra *et al* [13]. Tripathi [12] extended the Misra and Kleinman work to include the effect of localized moments and χ in his theory is expressed as

$$\chi = \chi_{MK} + P_{\chi loc} \quad (2)$$

Here, $P_{\chi loc}$ is the contribution due to the conduction electron and local moment hybridization. P is the EPR shift at the magnetic ion site. A reasonably complete expression for P was derived by the author. Many body effects were considered on all the constituents of χ_{MK} by Misra *et al* [13]. The theories reviewed above were applied to metals [14] and semiconductors [15–17]. On the subject of nuclear magnetism of Bloch electrons, a theory of the Knight shift was derived in the presence of spin-orbit and many-body effects by Tripathi *et al* [18]. This theory was applied to semiconductors [18–21] and metals [22,23] with reasonable success. Effect of indirect nuclear spin-spin interactions [24,25] were also considered on the Knight shift [26,27] by the author and his group.

4. Some recent advances in magnetic materials

A. Magnetic multilayers :

Study of magnetic multilayers constitutes an important subject in magnetism both for basic research and applied technology [28–30]. On the Physics side topics such as exchange coupling and transport in the presence of magnetic field are important; technologically these materials promise to be good magnetic storage devices. A magnetic multilayer system consists of a complex substrate S , followed by a periodic repetition – n times of a thickness x of ferromagnet X and a thickness y of a non-magnetic metal Y called the spacer. Typically, x and y of range from a few angstroms to a few hundred angstroms, and n can be as small as one and as large as several hundred. The multilayer system is usually indicated as $S[X(x)/Y(y)]_n$. Some typical substrates are Cu, Au, Cr, Mo, LiF, NaCl,

GaAs *etc.* The most commonly used ferromagnets are Fe, Co, Ni, Ni-Fe, Fe-Co, Dy, Gd *etc.* Cu, As, Au, Mg, Sn, V, Nb, Mo, Pd, Y are some of the most commonly used spacers. Two closely related effects appear in these systems : (1) Successive ferromagnetic layers, which are separated by spacers, arrange themselves in a ferromagnetic or antiferromagnetic coupling to each other. The magnetisation is usually in the planes of the layers. For a given system the coupling is an oscillatory function of thickness y of the spacers. (2) The second effect takes place in the samples in which the magnetic alignment is antiparallel. The application of strong enough magnetic field which is usually parallel to the plane of the layers, changes the arrangement of magnetisation. The AFM coupling is overcome and the magnetic moments of all the ferromagnetic layers are forced to lie in the same direction. Simultaneously the electrical resistance of the samples, both in the plane of layers and perpendicular to it, decreases. This decrease can be a few percent (small- ν magnetoresistance as in Co/Ru) or up to 65% (giant negative magnetoresistance, GMR as in Fe/Cr or Co/Cu). Phenomena such as GMR, TMR (tunnelling magnetoresistance), exchange bias, interface anisotropy and interlayer exchange coupling have given scientists a new tool box with which to construct remarkable new devices, and new phenomena such as spin electronics and magneto-electronics.

B. Half metallic magnets :

In the early 1980s, during a computational study of magnetic compounds, Rob de Groot [31] and collaborators discovered a new type of magnetic material with unusual characteristics in that only one of the two spin directions is metallic. To be more precise, electrons responsible for the metallic behaviour share the same spin; electrons with opposite spin are insulating. Combining metallic and insulating properties in a single system, half metals [32,33] can be thought of a new state of matter. The property can be exploited in possible applications as memory devices and computer processors. To be a half metallic magnet, the material must have a collinear magnetic arrangement with the following qualitatively different types of up and down band structure : one spin direction (let us say the up spin) has partially occupied bands, whereas the other (down-spin) has a precisely filled set of bands that are separated from unoccupied bands by a band gap. The upper most occupied energy level of the up-spins defines the system's Fermi level, which lies within the band gap of the spin-down electrons. Half metallic characteristics have been studied primarily in ternary compounds, specifically spinels,

such as Fe_3O_4 (FeFe_2O_4), Heuslers such as Co_2MnSi and half Heuslers such as NiMnSb . The binary compound CrO_2 is also a half metal. A more complicated half metallic oxide is $\text{Sr}_2\text{FeMoO}_2$. Dilute magnetic semiconductors (DMS) such as GaMnAs and HgMnSe form another class of half metal. Half metallicity has been probed by a variety of experimental techniques, including positron annihilation, optical spectroscopy and normal state transport. One of the characteristics of the half metal is that the magnetic moment should be an integer multiple of μ_B .

C. Spin transistor :

Magnetic research lagged behind semiconductor research because of relevant length scales. Cooperative magnetic behaviour derives from the electron exchange, the length scale of which is of the order of few atomic spacings. Thus magnetic material structures must be controlled at the scale of nanometer or less. Advances in the atomic scale growth triggered new magnetic phenomena. Spintronics or spin-electronics depends on the spin-polarized transport. A spin-transistor [34] is a three-terminal bipolar device consisting of a normal metal sandwiched between two ferromagnetic metal layers. Current is driven from the first ferromagnetic film (emitter) into the nonmagnetic metal (base) and back to the battery. A symmetric circuit arm connecting the second ferromagnetic film (collector) to the base contains a current detector. If the magnetic moments of the two ferromagnetic layers are parallel as shown in Figure 1(a), spin accumulation in the base will create an electric field that pushes current in the detector

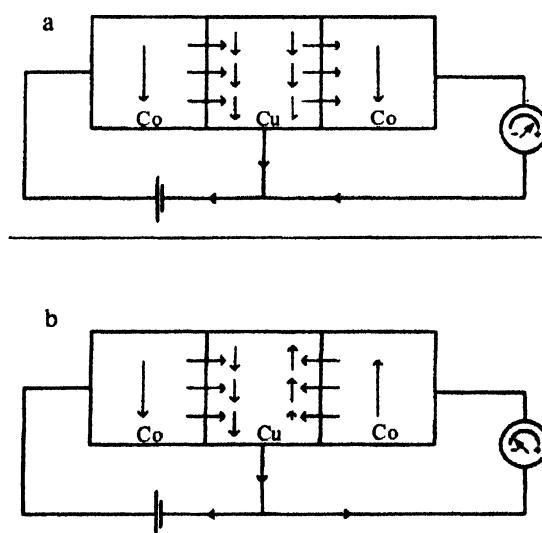


Figure 1. Current flow in the three-terminal bipolar device is shown for aligned (a) and antiparallel (b) magnetic moments in the two ferromagnetic films.

arm of the circuit. If, however, the magnetic moments are antiparallel, as shown in Figure 1(b), the spin-accumulation electric field at the base-collector interface has the opposite sign; current is pulled from the collector into the base and a negative current is generated in the detector arm. The current flow through the detector can thus undergo bipolar modulation by modulating the direction of the magnetisation in the second layer. The device may be thought of as a non-volatile computer memory element, storing information via the orientation of the second layer.

D. Ferromagnetism and superconductivity :

The coexistence of antiferromagnetism with superconductivity is known for quite some time. However, recently there has been some activity in the coexistence of ferromagnetism and superconductivity. UGe_2 [35] is a strong ferromagnet. However, under pressure, the f -bands broaden and magnetism is suppressed. The second material in which the coexistence of the ferromagnetism is found is ZrZn_2 [36]. The two components are individually paramagnetic superconductors, and the compound is weakly ferromagnetic. The Curie temperature, T_m is 25 K. Compressing the material pushes the atoms closer, making it closer for electrons to hop from atom to atom and broadening the energy bands. Broad bands do not favour magnetism, so pressure almost universally tends to make T_m go down and eventually vanish at the critical pressure p_c . The superconducting transition temperature is about 1 K. These are not the only materials in which the superconductivity exists in more or less close proximity to magnetism. The high T_c cuprates are almost antiferromagnets; the borocarbides that contain magnetic ions are fully antiferromagnetic; strontium ruthenate is almost a ferromagnet. Even iron itself, the archetypal ferromagnet has recently been found to be a superconductor [37], albeit under such high pressure that it ceases to be ferromagnetic. And in other compounds such as $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ and its fellow ruthenocuprates, ferromagnetism and superconductivity coexist at the same temperature and pressure, but in different atomic planes.

E. Photoinduced magnetism :

Light induced magnetism is a method by which spin-polarized carriers are created through interband excitations using circularly polarized light. The circularly polarized light interacts via exchange interaction with the magnetic ions in a diluted magnetic semiconductor or quantum wells involving these systems and induce a magnetic moment which is detected by sensitive squid methods. The phenomenon was first observed in $\text{Hg}_{1-x}\text{Mn}_x\text{Te}$ [38] and

then in $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ [39]. Mechanisms of Mn-spin orientations by photoelectrons brought about by s - d coupling are of two types. In the first case, the static polarization is caused by the mean field of the spin-polarized electrons and in the second case, there is a dynamic polarization caused by the s - d spin flip scattering. However dynamic polarization is strongly suppressed by interaction among Mn spins. The effect is observed in $\text{Cd}_{1-x}\text{Mn}_x\text{TeCd}_y\text{Mn}_y\text{Te}$ ($x \neq y$) in multiple quantum wells in 1989 [40]. Apart from II-VI based compounds, ferromagnetic order is observed in InMnAs/GaSb quantum wells. If $T_c < 35$ K, the order is preserved even when the light is switched off. The mechanism depends on hole transfer from GaSb to InMnAs [41]. On the other hand an opposite effect was observed in manganites, $(\text{Nd}_{0.5}\text{Sm}_{0.5})_{0.6}\text{Sr}_{0.4}\text{MnO}_3$, i.e. there is a photoinduced demagnetization. However, the spin-disordered state seems to be a metastable state, but finally collapses into a ferromagnetic state [42]. Apart from the dms and the quantum wells, recently photo induced magnetization was observed in organic-based (plastic) magnet $\text{Mn}(\text{TCNE})_x\text{y}(\text{CH}_2\text{Cl}_2)$ [43]. Here TCNE stands for tetracyanoethylene. When the material is exposed to blue light, its magnetization increases as much by 50%. The material is magnetic at $T < 75$ K, and retains its magnetization for days, perhaps through the formation of the metastable state in a distorted lattice. The magnetism is partially undone by green light. This kind of phenomenon can be used for information storage at low cost.

5. Conclusion

In this invited talk, a brief history of the development of magnetic phenomena and materials is given. Starting from the classical age, the article goes upto recent discoveries. A brief note about Indian contributions is also presented. Magnetism encompasses vast and complicated phenomena. It also abounds in useful materials. The choice of recent phenomena and materials is completely personal and this has been done in view of their importance, as evidenced by publications in leading journals. The nature of the article is a review with some reference to the author's original work.

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